

PATENT SPECIFICATION

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 (72) Inventor PETER WILLIAM AUSTIN

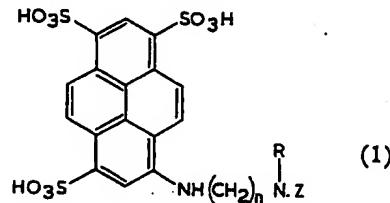


(54) REACTIVE PYRENE DYESTUFFS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to new reactive dyestuffs and more particularly to new reactive dyestuffs, preferably of bright fluorescent yellow shades.

15 According to the invention there are provided new reactive dyestuffs having the formula:



wherein

n has a value of 2 to 6

20 R represents H, an alkyl or hydroxyalkyl radical having up to 4 carbon atoms, and Z represents a cellulose-reactive group i.e. a group containing a substituent which reacts with cellulose in the presence of alkali.

25 As examples alkyl and hydroxyalkyl groups represented by R there may be mentioned methyl, ethyl, propyl, n-butyl and β -hydroxyethyl. However the preferred meaning of R is H.

30 The preferred value of n is 2.

As examples of cellulose-reactive groups represented by Z, there may be mentioned aliphatic sulphone groups which contain a sulphate ester group in β -position to the sulphur atom, e.g. the β -sulphatoethylsulphone group, α,β -unsaturated acyl radicals of aliphatic carboxylic acids for example, acrylic acid, α -chloroacrylic acid, propionic acid,

maleic acid and mono- and dichloro-maleic acids; also the acyl radicals of acids which contain a substituent which reacts with cellulose in the presence of an alkali, e.g. the radical of a halogenated aliphatic acid such as chloroacetic acid, β -chloro and β -bromo-propionic acids and α,β -dichloro- and dibromo-propionic acids. Other examples of cellulose or polyamide-reactive groups are tetrafluorocyclobutane carbonyl, trifluorocyclobutene carbonyl, tetrafluorocyclobuteneethenyl carbonyl, and heterocyclic radicals which contain 2 or 3 nitrogen atoms in the heterocyclic ring and at least one cellulose- or polyamide-reactive substituent on a carbon atom of the ring.

As examples of such heterocyclic radicals, there may be mentioned, for example

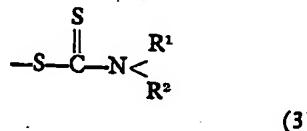
2:3 - dichloro - quinoxaline - 5- or -6 - sulphonyl, 40
 2:3 - dichloro - quinoxaline - 5- or -6 - carbonyl, 45
 2:4 - dichloro - quinazoline - 6- or -7 - sulphonyl, 50
 2:4:6 - trichloro - quinazoline - 7- or -8 - sulphonyl, 55
 2:4:7- or 2:4:8 - trichloro - quinazoline - 6 - sulphonyl, 60
 2:4 - dichloro - quinazoline - 6 - carbonyl, 65
 1:4 - dichloro - phthalazine - 6 - carbonyl, 70
 4:5 - dichloro - pyridaz - 6 - on - 1 - yl, 75
 2:4 - difluoro - 5 - chloropyrimid - 6 - yl,
 2:4 - dichloro - pyrimidine - 5 - carbonyl,
 2 - methyl - sulphonyl - 5 - chloro - 6 - methylpyrimid - 4 - yl,
 4(4:5 - dichloro - pyridaz - 6 - on 1 - yl) - benzoyl,
 4 - (4:5 - dichloro - pyridaz - 6 - on - 1 - yl)phenylsulphonyl,

and, more particularly s - triazin - 2 - yl and pyrimidin - 2 - yl or -4 - yl radicals which contain on at least one of the remaining 2-, 4- and 6-positions, a bromine or, preferably, a chlorine atom, a sulphonic acid group, a thiocyanato group, an aryloxy or aryl-

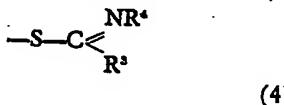
thio group containing an electronegative substituent such as sulphophenoxy, sulphonphenylthio, nitrosulphophenoxy, disulphophenoxy and sulphonaphthoxy, or a group of the formula:



wherein Y represents a group of atoms necessary to form a 5- or 6-membered heterocyclic ring which may carry substituents or form part of a fused ring system; or a quaternary ammonium or pyridinium group; or a group of the formula:



wherein R¹ and R² each represents the same or different alkyl, cycloalkyl, aryl or aralkyl group, or R¹ and R² together form, together with the nitrogen atom, a 5- or 6-membered heterocyclic ring; or a group of the formula:



wherein R³ and R⁴ may be the same or different and each represents a hydrogen atom or an alkyl, aryl or aralkyl group.

In the cases where the pyrimidine ring or triazine ring carries only one such reactive substituent, the said ring may have a non-reactive substituent on the remaining carbon atoms.

By a non-reactive substituent there is meant a group which is bound by a covalent bond to a carbon atom of the triazine or pyrimidine nucleus, which covalent bond is not ruptured under the conditions used for application of the reactive dye.

As examples of such substituents, there may be mentioned, for example, primary amino and hydroxyl groups, also mono- or di-substituted amino groups, etherified hydroxyl and etherified mercapto groups; in the case of substituted amino groups, this class includes for example, mono- and di-alkylamino groups in which the alkyl groups preferably contain at most 4 carbon atoms, and which may also contain substituents for example, hydroxyl or alkoxy groups, and phenylamino preferably sulphonated phenylamino which may be further substituted on the nucleus, e.g. by CH₃, OCH₃, CO₂H or Cl, or on the N atom e.g. by methyl, ethyl, hydroxyethyl or sulphonethyl, and naphthylamino groups preferably sulphonated naphthylamino containing up to 3 SO₃H

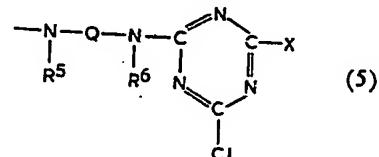
groups; in the case of etherified hydroxyl and mercapto groups, this class includes, for example, alkoxy and alkylthio groups preferably those of low molecular weight, i.e. having up to 4 carbon atoms and phenoxy, sulphonated phenoxy, phenylthio, naphthoxy or naphthylthio groups; as particular examples of all these classes there may be mentioned for example:

methylamino,	60
ethylamino,	
dimethylamino,	
β-hydroxyethylamino,	
di-(β-hydroxyethyl)-amino,	
β-chloroethylamino,	65
cyclohexylamino,	
anilino,	
o-, m- and p-sulphophenylamino,	
2,4-, 2,5- and 3,5-disulphophenylamino,	
N-methylsulphophenylamino,	70
N-β-hydroxyethylsulphophenylamino,	
mono-, di and tri-sulphonaphthylamino,	
4- and 5-sulpho-o-tolylamino,	
2-carboxyphenylamino and 5-sulpho-2-carboxyphenylamino,	75
N-ω-sulphonethylphenylamino,	
methoxy, ethoxy, and butoxy,	
phenoxy, p-sulphophenoxy and chlorophenoxy	
and phenylthio groups.	80

Chlorine atoms or cyano, nitro, carboxy and carbalkoxy groups in the 5-position of a pyrimidyl radical come into the category of non-reactive substituents.

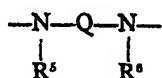
If desired, a non-reactive substituent may itself be the residue of a coloured amine, e.g. of the azo, anthraquinone or phthalocyanine series. Dyes of this kind have the basic bright yellow shade provided by the pyrene nucleus modified by the shade of the second chromophoric group.

Furthermore, a non-reactive substituent may contain a reactive grouping; into this category come, e.g. anilino or naphthylamino groups substituted by a β-sulphatoethylsulphonyl, β-sulphatoethylsulphonylaminio or β-chloroethylsulphonyl group, or more especially, di-amine radicals of the formula:



either wherein R⁵ and R⁶ independently represent H or alkyl or hydroxyalkyl radicals having up to 4 carbon atoms, and Q represents an aliphatic or aromatic linking group,

or



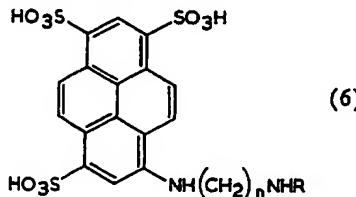
represents the *N,N'*-piperazinylene radical, and X represents Cl, OCH₃, NH₂ or an anilino or sulphonated anilino radical which may be further substituted by Cl, CH₃, OCH₃ or CO₂H or a sulphonated naphthylamine radical.

As examples of radicals represented by Q in formula (5) there may be mentioned alkylene, poly(alkyleneimine), or dialkyloxide radicals, e.g.

ethylene,
propylene,
15 tri-, tetra- and hexa-methylene,
—C₂H₄NHC₂H₄—
—C₂H₄(NHC₂H₄)₂—
—C₂H₄OC₂H₄—

20 or a divalent aromatic radical of the benzene or naphthalene series which preferably contains 1 or 2 SO₃H groups, e.g. a mono- or di-sulpho-*m*-phenylene, mono- or di-sulpho-*p*-phenylene or a disulphonaphthylene radical, or a divalent radical of the stilbene, diphenyloxide, diphenylmethane, diphenylurea, diphenoxoethane or diphenylamine series which preferably contains 1 or 2 SO₃H groups.

25 The invention also provides a process for manufacture of the new dyestuffs which comprises reacting a compound of the formula:



30 wherein the symbols R and n have the meanings stated above, with the anhydride or halide of an acid of which the acid radical contains a substituent capable of chemically reacting with the fibre to form a chemical bond, or a heterocyclic compound which contains a halogen atom attached to a carbon atom of the heterocyclic nucleus and also a reactive substituent of the kind just stated.

35 The above process can conveniently be carried out by stirring a mixture of the reactants in an aqueous medium at a suitable temperature, which may be from 0°C in the case of cyanuric chloride to 50°C or even higher in the case of less reactive acyl halides, anhydrides or heterocyclic compounds. As a general rule it is preferred to add an acid-binding agent during the course of the

reaction to maintain the pH within the limits 8 to 11.

The compounds of formula (6) used in the above process can in general be obtained by reacting pyrene-1,3,6,8-tetrasulphonic acid with a diamine of the formula:



e.g. by heating the tetrasulphonic acid with an aqueous solution of the diamine at a temperature of 200°C or higher in an autoclave whereupon one of the SO₃H groups is replaced by the radical of the diamine. As examples of the latter, there may be mentioned:

ethylene diamine,
1,3-propylenediamine,
1,6-hexylenediamine,
N-β-hydroxyethyl ethylenediamine,

As examples of halides or anhydrides of acids or heterocyclic compounds which may be used, there may be mentioned, for example, carbyl sulphate and the anhydrides or acid halides of α,β-unsaturated aliphatic acids such as chloromaleic anhydride, propiolyl chloride and acryloyl chloride, the acid chlorides of halogenated aliphatic acids, e.g.

chloroacetyl chloride,
sulphochloroacetyl chloride,
β-bromo- and β-chloro-propionyl chlorides,
α,β-dichloro- and dibromo-propionyl chlorides,
2,2,3,3-tetrafluorocyclobutane carbonyl chloride,
β-(2,2,3,3-tetrafluorocyclobutyl)acryloyl chloride,
2,3,3-trifluorocyclobut-1-ene carbonyl chloride,
β-(2,3,3-trifluorocyclobut-1-enyl)acryloyl chloride,

also heterocyclic compounds which contain at least 2 nitrogen atoms in the heterocyclic rings and which contain 2 or more halogen, especially chlorine atoms in the *ortho* position to the nitrogen atoms, e.g.

2:3 - dichloro - quinoxaline - 5- and -6- carbonyl chlorides,
2:3 - dichloroquinoxaline - 5- and -6- sulphonyl chlorides,
2:4 - dichloro - quinazoline - 6- and -7- sulphonyl chlorides,
2:4:6 - trichloro - quinazoline - 7- and -8- sulphonyl chlorides,
2:4:7- and 2:4:8 - trichloro - quinazoline- 6 - sulphonyl chlorides,
2:4 - dichloro - quinazoline - 6 - carbonyl chloride,
1:4 - dichloro - phthalazin - 6 - carbonyl chloride,

2:4 - dichloro - pyrimidine - 5 - carbonyl chloride,
 β - (4:5 - dichloro - pyridazonyl - 1 -)-propionyl chloride,
5 1 - (4' - chloroformylphenyl) - 4:5 - dichloro-6 - pyridazone,
1 - (4' - chlorosulphonylphenyl) - 4:5 - dichloro-6 - pyridazone,
10 2:4:6 - tribromo- and trichloro - pyrimidines,
2:4:6 - trifluoro - 5 - chloropyrimidine,
2:4:5:6 - tetrachloropyrimidine,
2 - methylsulphonyl - 4:5 - dichloro - 6 - methyl pyrimidine,
15 5 - methyl - 2:4:6 - trichloropyrimidine,
5 - nitro - 2:4:6 - trichloropyrimidine,
2:4 - dichloro - 5 - nitro - 6 - methyl pyrimidine,
2:4 - dichloro - 5 - nitropyrimidine,
20 2:4:6 - trichloro - 5 - cyanopyrimidine,
5 - ethoxycarbonyl - 2:4 - dichloropyrimidine,
2:4 - dichloropyrimidine - 5 - carbonyl chloride,
cyanuric bromide,
cyanuric chloride,
25 also the primary condensation products of cyanuric bromide or cyanuric chloride with ammonia, an alkali metal sulphite or thiocyanate or an organic mercaptan, hydroxy compound or an organic primary or secondary amine, for example:
methanol,
ethanol,
iso-propanol,
phenol,
35 *o*-, *m*- and *p*-chlorophenols,
o-, *m*- and *p*-cresols,
o-, *m*- and *p*-sulphophenols,
thiophenol,
thioglycolic acid,
40 di-methylthiocarbamic acid,
mercaptobenzthiazole,
thioacetamide,
methylamine,
dimethylamine,
45 ethylamine,
diethylamine,
n-propylamine,
iso-propylamine,
butylamine,
50 hexyl- and cyclohexyl-amines,
toluidine,
piperidine,
morpholine,
methoxyethylamine,
55 ethanolamine,
aminoacetic acid,
aniline-2:4-, 2:5- and 3:5-disulphonic acids,
orthanilic, metanilic and sulphanilic acids,
2-, 3- and 4-aminobenzoic acids,
60 4- and 5-sulpho-2-aminobenzoic acids,
4- and 5-sulpho-*o*-toluidines,
5-amino-2-hydroxybenzoic acid,
2-amino-ethanesulphonic acid,

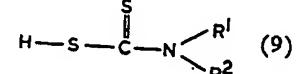
amino-naphthalene mono- and di-sulphonic acids,
N-methylaminoethane sulphonic acid,
m-aminophenyl- β -sulphatoethyl sulphone,
2-methoxy-5- β -sulphatoethyl sulphonyl aniline,
m- β -chloroethylaminosulphonyl aniline,

also the primary condensation products of cyanuric chloride with coloured amines, e.g. of the aminoazo, aminoanthraquinone or aminophthalocyanine series; also, the secondary condensation products of cyanuric chloride with:

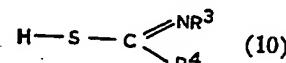
alkali metal sulphites,
alkali metal thiocyanates,
phenols and thiophenols,

containing an electronegative substituent, and compounds of the formulae:

H—S—C  (8)

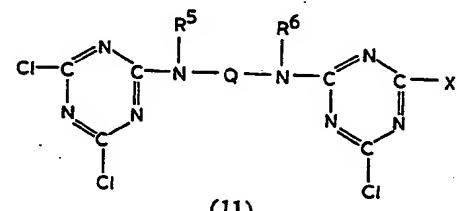
H—S—C  (9)

and

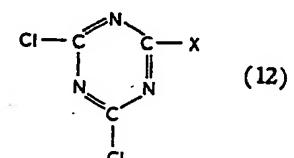
H—S—C  (10)

wherein Y, R¹, R², R³ and R⁴ have the meanings stated above.

Reactive groups of formula (5) above can be introduced by using a bis-triazinyl diamine of the formula:

 (11)

wherein R⁵, R⁶, Q and X have the meanings stated in connection with formula (5) i.e. the condensation product of 2 moles of cyanuric chloride, or of 1 mole of cyanuric chloride and 1 mole of a triazine of the formula:

 (12)

with one mole of a diamine of formula



As examples of diamines of formula (13), there may be mentioned:

5 piperazine,
aliphatic diamines, e.g. alkylene diamines and other α, ω -diamino aliphatic compounds, e.g.
10 ethylene diamine,
1,2- and 1,3-propylene diamines,
1,6-hexylene diamine,
diethylene triamine,
triethylene tetramine,
di-(β -aminoethyl) ether,
15 aromatic diamines of the benzene and naphthalene series, more especially those containing 1 or 2 SO_3H groups, e.g.:
m- and p-phenylenediamine,
1,3 - phenylenediamine - 4 - sulphonic and
4,6 - disulphonic acids,
20 1,4 - phenylenediamine - 2 - sulphonic and
2,5 - disulphonic acids,
2,6 - naphthylene diamine - 4 - sulphonic
and 4,8 - disulphonic acids,
25 1,5 - naphthylene diamine - 2- and 4-sul-
phonic and 3,7 - disulphonic acids,
4,4' - diaminodiphenyl - 2 - sulphonic and
2,2' - disulphonic acids,
4,4' - diaminostilbene - 2,2' - disulphonic
acid,
30 4,4' - diaminodiphenylurea - 2,2' - and 3,3'-
disulphonic acids,
4,4' - diaminodiphenylamine - 2,2' - disul-
phonic acid,
4,4' - diaminodiphenoxethane - 2,2' - disul-
phonic acid,
35 4,4' - diaminodiphenylmethane - 2,2' - disul-
phonic acid,
4,4' - diaminoazobenzene - 2 - sulphonic and
2,2' - disulphonic acids,
40 N - methyl and N - ethyl - 1,4 - phenylene-
diamine - 2 - sulphonic acids
N - (β - hydroxyethyl)ethylene diamine.

The dyes of formula (1) wherein the cellulose-reactive group Z is a *s*-triazine nucleus substituted by a chlorine or bromine atom and an amino or substituted amino group can also be obtained by reacting a cellulose-reactive dye of formula (1) in which Z is a dichloro- or dibromo-*s*-triazine group with ammonia or an amine.

The cellulose-reactive dyes of formula (1) wherein the cellulose-reactive group is a *s*-triazine nucleus substituted by SO_3H , a quaternary ammonium group or a group of formulae (2), (3) and (4), can be obtained by reacting a cellulose-reactive dye of formula (1) containing a *s*-triazine group substituted by at least one chlorine or bromine

atom with an alkali metal salt of sulphurous acid, a tertiary amine or a compound of formulae (8), (9) and (10).

These reactions also may be carried out by stirring the reactants together in an aqueous medium at a suitable temperature which, in general, will be within the range of 30-95° C., and maintaining the pH at an appropriate value by addition of an acid-binding agent. In the case where ammonia or amine is the reactant, an excess can be used to act as acid-binding agent. Otherwise, sodium carbonate or sodium hydroxide may conveniently be used as acid-binding agent.

The dyes of formula (1) in which Z represents a group of formula (5) may also be obtained by reacting a dyestuff of formula (1) in which Z represents the dichloro-*s*-triazine radical with one mole of a diamine of formula (13) and subsequently reacting the product with one mole of a *s*-triazine compound of formula (12).

The new dyestuffs may be used for the colouration of a variety of textile materials, for example, natural proteins such as wool, silk and leather, superpolyamides and, more especially natural or regenerated cellulose textile materials such as cotton, linen and viscose rayon. For colouring the cellulose materials the dyestuffs are preferably applied by printing or dyeing the material in conjunction with a treatment with an acid-binding agent, e.g. caustic soda, sodium carbonate, sodium triphosphate or sodium silicate, which may be applied to the textile material before during or after the application of the dyestuff. When so applied the new dyestuffs react with the cellulose and yield primarily brilliant fluorescent greenish-yellow shades of excellent fastness to washing; other shades are obtained where a different chromophore is linked to the cellulose-reactive group. In contrast to azopyrazolone or azopyridone dyes of similar shade, the new dyes are distinguished by their fastness to washing in the presence of hypochlorite bleach and their fastness to oxidative coppering.

The invention is illustrated but not limited by the following examples in which parts are by weight:

Example 1.
105 Parts of the tetrasodium salt of pyrene-1,3,6,8-tetrasulphonic acid and 1300 parts of a 65% aqueous solution of ethylene diamine are heated in an autoclave at 200-210° for 18 hours. The solution is cooled and the excess ethylene diamine removed by evaporation. The residual material is dissolved in 400 parts of water, charcoal treated, screened and added to a stirred solution of 80 parts of potassium acetate in 3000 parts of methylated spirits. The resulting yellow precipitate is collected by filtration and dried (90 parts). (Found N = 4.8%. $\text{C}_{18}\text{H}_{13}\text{K}_3\text{N}_2\text{O}_9\text{S}_3$ requires N = 4.6%).

10 Parts of this product are dissolved in 200 parts of water, cooled to 5° and 50 parts of ice and 1 part of calsoene oil are added. 5 Parts of cyanuric chloride dissolved in 15 parts of acetone are then added and the suspension is stirred at 0—5°, pH 9—9.5 for $\frac{1}{2}$ hour. It is then filtered, the pH lowered to 6.5 by dropwise addition of 2N hydrochloric acid, and 2 parts of potassium dihydrogen acid, and 2 parts of potassium dihydrogen *ortho* phosphate and 1 part of disodium hydrogen *ortho* phosphate are added. The solution is then evaporated to dryness at less than 40°. The resulting dyestuff, when applied to cellulosic fibres in the presence of an acid-binding agent, yields bright (fluorescent) greenish-yellow shades of good fastness to washing, washing in the presence of hypochlorite, and oxidative coppering.

Example 2.

20 66 parts of the tetrasodium salt of pyrene-1,3,6,8-tetrasulphonic acid, 256 parts of N- β -hydroxyethylmethylenediamine and 70 parts of water are heated at 220° C for 20 hours in an autoclave. The resulting solution is allowed to cool and then evaporated to dryness *in vacuo*. The residual syrup is dissolved in 500 parts of water, treated with charcoal, filtered and re-evaporated to dryness. Slurrying with 300 parts of methylated spirits (74° over proof) and 30 parts of potassium acetate gives a brownish-yellow solid which is collected by filtration and dried. (Found: N = 4.5%. $C_{21}H_{14}K_3N_2O_{10}$ requires N 5%).

25 6 Parts of this product are dissolved in 200 parts of water, 100 parts of ice and 1 part of a dispersing agent are added and stirred vigorously at 0—5°, pH 9—10 whilst a solution of 3 parts of cyanuric chloride in 10 parts of acetone is added. The mixture is stirred for $\frac{1}{2}$ hour at 0—5°, pH 9—10, then filtered and neutralised to pH 6.5 by the dropwise addition of 2N hydrochloric acid. A solution of 0.66 parts of potassium dihydrogen *orthophosphate* and 0.33 parts of disodium hydrogen *orthophosphate* in 10 parts of water is added and the solution evaporated to dryness at less than 40°. The solid residue (9 parts) is finally dried *in vacuo* over phosphorus pentoxide. When applied to cellulosic fibres in conjunction with an acid binding agent, the dyestuff colours the fibres in bright (fluorescent) yellow shades fast to washing.

30 Further examples of the invention are described in the table in which the product obtained by condensing pyrene-1,3,6,8-tetrasulphonic acid with the diamine named in column 2 is reacted with the agent named in column 3. The shades of the derived dyestuffs on cellulose are bright greenish-yellow, often fluorescent; "dct" refers to 2,4-dichloro-s-triazine.

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Example	Diamine	Acylating Agent
3	1,3-diaminopropane	6-anilino-dct
4	Ethylene diamine	6-methoxy-dct
5	"	2,4,6-trichloropyrimidine
6	"	2,4,5,6-tetrachloropyrimidine
7	1,6-diaminohexane	5-cyano-2,3,6-trichloropyrimidine
8	N-methylethylenediamine	carbyl sulphate
9	N-ethyl-1,3-diaminopropane	2,3-dichloroquinoxaline-5-carbonyl chloride
10	1,4-diaminobutane	6-(N- <i>ω</i> -sulphomethylanilino)-dct
11	N- β -hydroxyethyl ethylene diamine	6-(<i>p</i> -sulphoanilino)-dct
12	ethylene diamine	2,3-dichloroquinoxaline-6-carbonyl chloride
13	1,6-diaminohexane	6-(<i>m</i> -sulphoanilino)-dct
14	ethylene diamine	1,4-dichlorophthalazine-6-carbonyl chloride
15	"	2,4-dichloropyrimid-5-yl carbonyl chloride
16	1,5-diaminopentane	6-(4'- β -sulphatoethylsulphonyl anilino)-dct
17	N-methyl-1,6-diaminohexane	6-(3',5'-disulphonanilino)-dct
18	N-methyl-1,3-diaminopropane	6-(3'- β -sulphatoethylsulphonyl-anilino)-dct
19	Ethylene diamine	4-(4',5'-dichloropyridaz-6'-on-1'-yl)zoyl chloride
20	N- β -hydroxyethyl ethylene diamine	6-(5'-sulphonaphth-2'-ylamino)-dct
21	"	4-(4,5'-dichloropyridaz-6'-on-1'-yl)phenyl sulphonyl chloride
22	Ethylene diamine	6-isopropoxy-dct
23	"	2,4,6-trifluoro-5-chloropyrimidine
24	N-methylethylenediamine	6-(6'-sulphonaphth-2'-ylamino)-dct
25	Ethylene diamine	5-bromo-2,4,6-trichloropyrimidine
26	"	4,5-dichloro-6-methyl-2-methylsulphonyl pyrimidine
27	1,3-diaminopropane	6-(<i>o</i> -sulphoanilino)-dct

Example	Diamine	Acylating Agent
28	Ethylene diamine	β -chloroethylsulphonyl-endo-methylene cyclohexane carbonyl chloride
29	"	2,2,3,3-tetrafluorocyclobutane carbonyl chloride
30	"	2,3,3-trifluorocyclobut-1-ene carbonyl chloride
31	N- β -hydroxyethyl-1,3-diaminopropane	6-(2',5'-disulphoanilino)-dct
32	Ethylene diamine	β -(2',2',3',3'-tetrafluorocyclobutyl)-acryloyl chloride
33	Ethylene diamine	β -(2',3',3'-trifluorocyclo-but-1-enyl)acryloyl chloride
34	1,4-diaminobutane	6-ethyamino-dct
35	"	2,3-dichloroquinoxaline-6-carbonyl chloride
36	Ethylene diamine	2,3-dichloroquinoxaline-6-sulphonyl chloride
37	"	2,4,6-trichloroquinazoline-7-sulphonyl chloride
38	"	2,4,6-trichloroquinazoline-8-sulphonyl chloride
39	1,5-diaminopentane	6-(5',7'-disulphonaphth-2'-ylamino) dct
40	Ethylene diamine	2,4,7-trichloroquinazoline-6-sulphonyl chloride
41	"	2,4,8-trichloroquinazoline-6-sulphonyl chloride
42	1,3-diaminopropane	6-[3'-{6"-amino-4"-chloro-s-triazin-2"-ylamino}-4'-sulphophenylamino]-dct
43	1,6-diaminohexane	4,4'-bis-[2",4"-dichloro-s-triazin-6"-ylamino]-diphenyl urea-2,2'-disulphonic acid ($\frac{1}{2}$ mole)
44	N-methylethylenediamine	4,4'-Bis-[2",4"-dichloro-s-triazin-6"-ylamino]-diphenoxymethane-2,2'-disulphonic acid ($\frac{1}{2}$ mole)
45	1,4-diaminobutane	2,5-Bis-[2',4'-dichloro-s-triazin-6'-ylamino]-benzene-1,4-disulphonic acid ($\frac{1}{2}$ mole)

Example	Diamine	Acyliating Agent
46	Ethylene diamine	4,6-Bis-[2',4'-dichloro-s-triazin-6'-ylamino]-benzene-1,3-disulphonic acid (1 mole)
47	N- β -hydroxyethyl ethylene diamine	6-[4'-{6'''-(3'''-sulphophenyl-amino)-4'''-chloro-s-triazin-2'''-ylamino}-3'-sulphophenylamino]-dct

Example 48.

5 6.4 parts of the dyestuff obtained as described in Example 1 are stirred at 30° for 1 hour with 50 parts of water and 5 parts of ammonia solution (s.g. 0.88) and the solution then evaporated to dryness. The yellowish powder so obtained is found to colour cellulosic fibres, when applied in the presence of an acid-binding agent, in greenish-yellow shades showing good fluorescence, wash fastness, fastness to washing in the presence of chlorine and resistance to oxidative coppering.

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Further examples of the invention are described in the following table in which the compound prepared by condensation of pyrene-1,3,6,8-tetrasulphonic acid with the diamine described in column 2 is allowed to react first with cyanuric chloride and then with the compound named in column 3. The derived dyestuffs give bright greenish-yellow dyeings on cellulosic fibres characterised, in general, by good wet fastness and vivid fluorescence.

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Example	Diamine	
49	1,3-diaminopropane	Phenol
50	Ethylene diamine	Metanilic acid
51	..	2-aminotoluene-4-sulphonic acid
52	..	<i>o</i> -Toluidine
53	1,6-Diaminohexane	4-hydroxybenzoic acid
54	N- β -hydroxyethyl ethylene diamine	<i>o</i> -anisidine
55	..	6-hydroxynaphthalene-2-sulphonic acid
56	1,4-diaminobutane	4-aminobenzoic acid
57	N-methylethylene diamine	Taurine
58	N-ethyl-1,3-diaminopropane	4,4'-diaminostilbene-2,2'-disulphonic acid (½ mole)
59	Ethylene diamine	3,7-diaminonaphthalene-1,5-disulphonic acid (½ mole)
60	..	4,4'-diaminodiphenylsulphide-2,2'-disulphonic acid (½ mole)
61	..	4,4'-diaminodiphenyl-2,2'-disulphonic acid (½ mole)

Example 62.

6.5 parts of the dyestuff made as described in Example 48 are stirred at 60° with 100 parts of water, 3 parts of pyridine and 2 parts of sodium sulphite, until sulphiting is complete as judged by estimation of liberated sodium chloride. The solution is evaporated to dryness at 40° *in vacuo* to yield a yellowish-brown powder. When applied to cellulosic fibres in conjunction with an acid-binding agent, the product dyes the fibres in bright greenish-yellow shades fast to washing.

Example 63.

To a solution of 7 parts of the dyestuff obtained as described in Example 50 in 100 parts of water are added 3 parts of trimethylamine in 10 parts of water. The solution is stirred at 20° for 30 minutes, after which time the dyestuff is obtained by evaporating the solution to dryness *in vacuo*. When applied to cellulosic textiles in admixture with an acid binding agent it yields bright greenish-yellow shades fast to washing.

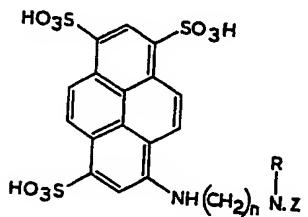
The trimethylamine can be replaced by an equivalent quantity of diazabicyclooctane to give a dyestuff of similar shade and properties.

Example 64.

To a solution of 7 parts of the dyestuff obtained as described in Example 50 in 100 parts of water are added 3.3 parts of pyridine in 10 parts of water and the solution is stirred at 80—90° for 1 hour before being evaporated to dryness *in vacuo*. The obtained dyestuff colours cellulosic dyestuffs.

WHAT WE CLAIM IS:—

1. A dyestuff of the formula



wherein

n has a value of 2 to 6

R represents H or a C₁—C₄ alkyl or hydroxalkyl radical, and

Z represents a cellulose-reactive group as herein defined

2. A dyestuff as claimed in claim 1 wherein

45 R represents H.

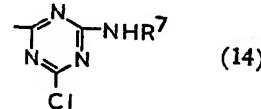
3. A dyestuff as claimed in claims 1 or 2 wherein n has a value of 2.

4. A dyestuff as claimed in claim 1, 2 or 3 wherein Z represents a heterocyclic group containing 2 or 3 nitrogen atoms and having at least one cellulose reactive substituent.

50 5. A dyestuff as claimed in claims 1, 2, 3

or 4 wherein Z represents a *s*-triazine ring having at least one chlorine atom.

6. A dyestuff as claimed in claims 1, 2, 3, 4 or 5 wherein R represents H, n has a value of 2 and Z represents a group of the formula



wherein R' represents H, phenyl, sulphophenyl, methylphenyl or methylsulphophenyl.

7. A dyestuff as claimed in claim 1 and hereinbefore described in any of the Examples.

8. A process for manufacturing the dyestuffs claimed in claim 1 which comprises reacting a compound of the formula



wherein n and R have the meanings stated in claim 1, with the chloride or anhydride of an acid the radical of which has a substituent capable of chemically reacting with the fibre to form a chemical bond, or a heterocyclic compound which has a halogen atom attached to a carbon atom of the heterocyclic ring and has a fibre-reactive substituent capable of chemically reacting with the fibre to form a chemical bond.

9. A process for the manufacture of dyestuffs claimed in claim 1 wherein the cellulose reactive group Z is a *s*-triazine ring substituted by chlorine or bromine and an amino or substituted amino group which comprises reacting a dyestuff as defined in claim 1 wherein Z is a dichloro- or dibromo-*s*-triazine ring with ammonia or an amine.

10. A process for the manufacture of dyestuffs claimed in claim 1 wherein the cellulose reactive group Z is a *s*-triazine ring substituted by SO₃H, a quaternary ammonium group or a group (2) (3) or (4) as hereinbefore defined which comprises reacting a dyestuff as defined in claim 1 wherein Z is a *s*-triazine ring substituted with at least one chlorine or bromine atom with an alkali metal salt of sulphurous acid, a tertiary amine or a compound of formula (8), (9) and (10) as hereinbefore defined wherein Y represents a group of atoms necessary to form a 5- or 6-membered heterocyclic ring which may carry substituents or form part of a fused ring system, R¹, R², R³ and R⁴ represent the same or different alkyl, cycloalkyl, aryl or alkaryl groups or R¹ and R² together with the

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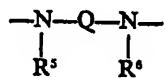
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nitrogen atom may form part of a heterocyclic ring.

11. A process for manufacturing a dyestuff as claimed in claim 1 wherein the cellulose reactive group Z consists of an *s*-triazine group substituted with a chlorine atom and a group of formula (5) as hereinbefore defined which comprises reacting a diamine of formula (13) as hereinbefore defined with, in either order, 1 mol of a dyestuff as defined in claim 1 wherein Z is a dichloro-*s*-triazine group and 1 mole of triazine of formula (12) as hereinbefore defined, wherein R⁵ and R⁶ independently represent H or C₁—C₆ alkyl or hydroxyalkyl radicals, Q represents an aliphatic or aromatic linking group or



represents the N,N'-piperazinylene radical and X represents Cl, OCH₃, NH₂ or an anilino or sulphonated anilino radical which may be further substituted by Cl, CH₃, OCH₃ or CO₂H or a sulphonated naphthylamine radical.

12. A process as claimed in any of claims 8—11 substantially as hereinbefore described with reference to or as illustrated by any of the Examples.

13. A process for colouring cellulose textile material which comprises dyeing or printing the material with a dyestuff as claimed in claim 1 in conjunction with a treatment with an acid binding agent.

14. Cellulose textile materials when coloured by the process claimed in claim 13.

BENJAMIN T. SMITH,
Agent for the Applicants.

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